Experimental Analysis and Modeling of NO_x Emissions in Compression Ignition Engines Fueled with Blends of Diesel and Palm Oil Biodiesel

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Keywords: Compression Ignition Engine, Modeling, NO_x Emissions, Blends, Diesel, Biodiesel.

Abstract: In this work, theoretical and experimental studies about the effects of the blends of diesel and palm oil biodiesel on NO_x formation in compression-ignition engines were developed. Experiments were conducted using commercial diesel, palm oil biodiesel and blends at 5% (B5), 20% (B20) and 50% (B50) as fuels. A phenomenological semi-empirical model that uses the information obtained from thermodynamic diagnostics was used for determining the theoretical NO_x formation. The model shows the high sensitivity of NO_x formation to the temperature and the operating conditions. Effects associated to the operating conditions of the engine were evaluated and the results indicate that high engine loads and low speeds lead to the NO_x formation. However, it was not possible to determine with precision, the effect of the type of fuel, because of the high sensitivity of the NO_x formation with respect to the operating conditions of the engine.

1 INTRODUCTION

Nowadays, biodiesel has received considerable attention given its potential use as a substitute for petroleum diesel. In general terms, the current technology is easily adapted for the use of such a fuel, since its implementation does not require significant changes in the control strategy of diesel engines. Biodiesel is a renewable fuel that reduces greenhouse emissions, such as particulate matter, carbon monoxide, and total hydrocarbons among others (Agudelo et al., 2010) (Sun et al., 2010).

However, the effect of the biodiesel and its blends with diesel fuel on NO_x formation is still a topic of discussion in the literature. (Lapuerta et al., 2008) and (Sun et al., 2010) classify the literature regarding the effect of the biofuels on NO_x production in five groups: group 1: NOx increase, group 2: NO_x increase under certain operating conditions and blends, group 3: little or no difference, group 4: NO_x decrease and group 5: uncertain or no comment. The increase in NO_x emissions generates serious problems for public health and the environment as these chemical species contribute to the production of ozone. High levels of ozone at low altitude cause respiratory diseases and damage to the vegetation among others. On the other hand, nitric oxides increase the level of acid rain and contribute to the production of photochemical smog (Turns, 1996). Also, NO_x affects the development of the biofuels industry due to the stringent restrictions for these emissions in American and European regulations. Several factors could increase or decrease the NO_x formation in blends of diesel and biodiesel: adiabatic flame temperature, ignition delay (Eckerle et al., 2009) and injection timing, as well as fuel chemistry (Ban-Weiss et al., 2007). These factors are determinant in the process of NO_x formation and should be analyzed as an overview rather than as individual effects (Ban-Weiss et al., 2007). Adiabatic flame temperature is affected by the fuel chemistry. Increased aromatic content produces higher flame temperatures that can promote NO_x formation through the thermal mechanism. This effect is most significant for modes of combustion dominated by diffusion, which mainly occur a high engine load operation (Eckerle et al., 2009).

Ignition delay is defined as the time between the start of injection and start of combustion; this parameter is generally shorter for biodiesel compared to petroleum diesel (Sun et al., 2010). The cetane

Quiceno, A., Quintero, R., Merola, S., Irimescu, A. and Valentino, G.
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In *Proceedings of the International Conference on Vehicle Technology and Intelligent Transport Systems (VEHITS 2016)*, pages 245-252
ISBN: 978-989-758-185-4

number is an indicator of the ignition delay time; higher values correspond to shorter ignition delay times (Ban-Weiss et al., 2007). It has been reported that the sensitivity of NO_x to changes in Cetane number is higher at low load than at high load (Lapuerta et al., 2008) which could reduce NO_x emissions at low load. Advanced injection timing could produce higher NO_x emissions as the combustion stars earlier, and thus the residence time of the burning mixture in the cylinder is increased. An advance in injection timing for biodiesel with respect to petroleum diesel is caused by its higher bulk modulus of compressibility for the biodiesel (Ban-Weiss et al., 2007).

In this paper, a theoretical and experimental analysis of the NO_x production using diesel and palm oil biodiesel blends is discussed The mechanism of formation of NO_x through the thermal mechanism is presented and a semi-empirical model is applied to determine the NO_x formation in the combustion diffusion phase.

2 METHODOLOGY

2.1 Modeling of NO_x Emissions in Diesel Engines

During combustion of fuels that do not contain nitrogen in their structure, nitrogen monoxide (NO) is formed from three mechanism: the thermal (Zeldovich), the prompt (Fenimore) and fuel-bound nitrogen (Sun et al., 2010). The thermal mechanism is presented during high temperatures in the combustion chamber when the reaction between the oxygen and the nitrogen is carried out (Miller and Bowman, 1989). The thermal mechanism represents the most important source in the NO_x formation (Ban-Weiss et al., 2007) and it is represented by three reactions: $O + N_2 \leftrightarrow NO + N$, $O + O_2 \leftrightarrow NO + O$ and $O + OH \leftrightarrow NO + H$ (Sun et al., 2010). Some simplifications have been applied to these equations in order to obtain the general dynamic expression for NO_x production presented as $d[NO] / dt = 6 \cdot 10^{16} / T^{0.5} \exp(-69.09 / T) \cdot [O_{2,eq}]^{0.5} \cdot [N_{2,eq}]$ (Sun et al., 2010) (Fernando et al., 2006) (Park et al., 2013). The first assumption is that the nitrogen chemistry can be de-coupled from combustion reactions due to the reactions rate of non-nitrogenated species generally occur much faster than that of the nitrogen chemistry, The second approach implies that the concentrations of O, O_2, OH, H and N_2 can be approximated to the equilibrium temperature. Finally, it is assumed that the radical N is in its steady state. An approach for solving the equation for calculating $d[NO]$ consists in applying a calculation scheme that takes into account the main kinetics aspects for the formation and destruction of NOx in the combustion chamber, which is linked to the engine operating conditions. The main variables include the instant pressure in the combustion chamber, the fuel mass burned rate (FMB), the adiabatic flame temperature (T_{ad}) and the heat release rate (HHR) which are obtained from thermodynamics diagnostics (Timoney et al., 2005) (Park et al., 2013) (Guardiola et al., 2011).

Based on the model developed by (Dec, 1997), it is possible to confirm that the premixed combustion phase does not show NO_x formation as the higher equivalent ratio reduces the amount of available oxygen. This situation implies that the most important processes for NO_x formation occur in the flame front during the combustion by diffusion.

Bearing this in mind, the theoretical NO_x production is determined in the combustion diffusion phase and the adiabatic flame temperature is the characteristic temperature. The combustion diffusion phase is taken from the values of heat release rate curves between the start of combustion (SOC) and the end of diffusion phase (EOD) (Timoney et al., 2005). The approximated values of adiabatic flame temperature for the biodiesel and their blends with diesel are taken from (Glaude et al., 2010). The equilibrium concentrations are estimated under stoichiometric conditions and constant pressure. The NASA simulation program "Chemical Equilibrium Program" was used for calculating the equilibrium concentrations.

Taking into account all the above considerations (Timoney et al., 2005), a final expression for the determination of NOx in each operating point is as follows: $e_{NOx} = k\, \Sigma_{SOC}^{EOC}\, T_{ad}^{0.5} \cdot \Delta FMB \cdot n^{-1} \cdot P^{-1} \cdot \exp(-0.69 / T_{ad}) \cdot [O_{2,eq}]^{0.5} \cdot [N_{2,eq}] \cdot \Delta CAD$, where constant $k = Ru\, 6 \cdot 10^{16} \cdot (1 + SFAR) / (6\, NSTEP\, M\, W_b)$, with FMB calculated based on the rate of heat release, with the lower heating value of each fuel NSTEP and ΔCAD corresponding to the angular resolution.

2.2 Experimental Setup

Test were carried out in a bench-mounted and instrumented automotive diesel engine (Table 1). The engine was coupled to a 230 kW Eddy current dynamometer. Air and fuel consumptions were measured with a hot-wire sensor and an electronic balanced mass flow sensor, respectively. NO_x were measured with chemiluminescense analyzer. In-cylinder combustion diagnostics was carried out using a two species (air and combustion products), single-zone model, based on the approach proposed by (Lapuerta et al., 1999). For recording the instantaneous in-cylinder pressure, a piezoelectric pressure transducer installed on the glow plug and a Kistler 5011B charge amplifier were used. The instantaneous piston position was determined using an angular encoder with a resolution of 1024 pulses/revolution coupled to the crankshaft at the opposite end of the fly-wheel. The angle of start of injection was measured with a clamp-on transducer.

Table 1: Engine specifications.

Reference	ISUZU 4AJ1
Type	Turbocharged, direct injection, rotating pump
Swept volume	2499cm^3
Configuration	4 in-line cylinders
Bore x stroke	93mm x 92mm
Compression ratio	18.4
Rated Power	59kW at 4100 rpm
Maximum torque	170Nm at 2300 rpm

Tests were performed using palm oil biodiesel (BP100), commercial grade diesel fuel and three diesel biodiesel blends (BP5, BP20, BP50). The properties of fuels are presented in Table 2. For each fuel, twelve operation modes, each one characterized by an effective torque (20, 40, 60 and 80 Nm) and engine speed (2000, 2250 and 2500 rpm) were tested, with NO_x emission measurements performed in steady state conditions.

3 RESULTS AND ANALYSIS

3.1 Experimental Analysis of NO_x Emissions

In Table 3, the experimental results of the NO_x measurements at different operating conditions and blends of diesel and palm oil biodiesel are presented. The trends in NO_x emissions were evaluated using statistical software. The Analysis of variance (ANOVA) shown in Table 4 and the confidence intervals given in Table 5 indicate that the type of biodiesel, speed and torque affect significantly on the NO_x emissions.

Figure 1 (a) suggests that the NO_x formation decreases with an increase of the engine speed for all fuels in all torque settings. Two factors could produce this trend, the mean temperature in the combustion chamber and the residence time of combustion gases. Table 6 shows the highest mean temperatures within the combustion chamber for all operation modes and fuel blends. Although the mean maximum temperature increases with the engine speed at the same load, the time of the residence of the combustion gases decreases leading to low values of NO_x in the range of speeds evaluated.

It is important to highlight at this point, that in the work of (Agudelo et al., 2010) it was observed that the NO_x increases with the speed of the engine in regions near to the maximum torque of the engine (i.e. 170 Nm at speeds lower than 1750 rpm).

As it can be seen in Figure 1(b), The NO_x formation increases as the Torque goes up. This

Table 2: Fuel properties.

Fuel	Chemical Formula[b]	Molecular weight[b] [kg/kmol]	Density at 15°C [kg/m^3]	Lower Heating Value [kJ/kg][a]	Stoichiometric air/fuel ratio $(SAFR)$[c]
Diesel	$C_{14.827}H_{29.032}O_{0.076}$	208.2	853.4	41568	14.8
BP100	$C_{18.050}H_{34.9}O_2$	283.5	879.7	37920	12.8
BP005	$C_{14.981}H_{29.258}O_{0.15}$	211.1	854.7	41444	14.5
BP020	$C_{15.340}H_{29.965}O_{0.382}$	220.1	858.7	41075	14.2
BP050	$C_{16.20}H_{31.53}O_{0.89}$	237.3	866.6	40387	13.9

[a] calculated from ultimate composition and measured gross heating value
[b] calculated from fatty acid methyl esters profile
[c] calculated from composition

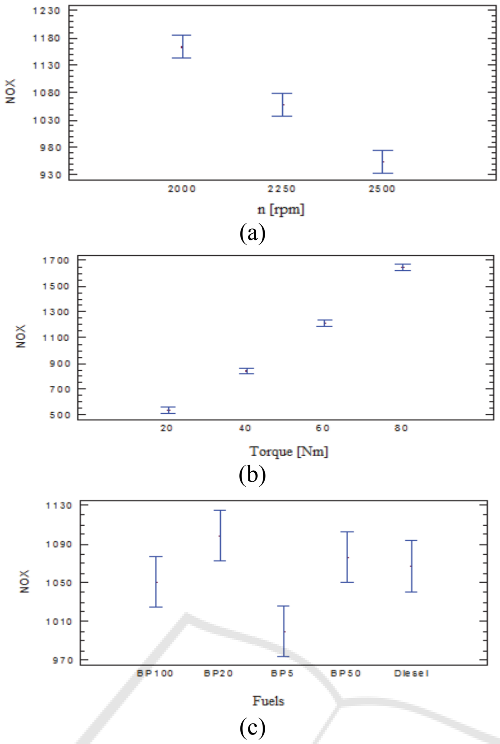

Figure 1: Results of variance analysis for NO_x. Means and 95% of Fisher LSD.

Table 3: NO_x emissions at different operating conditions and blends of biofuels.

		NO_x emissions [ppm]				
Torque [Nm]	n [rpm]	Diesel	BP5	BP20	BP50	BP100
20	2000	568	601	619	602	565
	2250	537	516	566	564	497
	2500	468	485	491	491	486
40	2000	940	897	979	956	856
	2250	854	867	862	836	805
	2500	753	759	802	724	730
60	2000	1358	1159	1412	1402	1359
	2250	1234	1089	1247	1228	1183
	2500	1089	1079	1111	1105	1092
80	2000	1827	1508	1879	1900	1898
	2250	1663	1631	1682	1646	1646
	2500	1515	1409	1534	1461	1495

Table 4: Variance analysis for NO_x emissions.

Source	Sum of squares	Gl	Medium square	F-Ratio	P-Value
Principal effects					
A Fuel	65783,6	4	16445,9	4,03	0,0066
B:[rpm]	442289,	2	221144,	54,19	0,0000
C:Torque [Nm]	1,03112E7	3	3,43708E6	842,22	0,0000
Residuals	204049,	50	4080,98		
Total (Correction)	1,10234E7	59			

Table 5: Mean and least squares for NO_x emissions with confidence intervals of 95%

Level	Cases	Means	Error Est.	Lower Bound	Upper Bound
Means Global	60	1058.62			
Fuel					
BP100	12	1051.0 (1.51%)	18.4413	1013.96	1088.04
BP20	12	1098.67 (-2.86%)	18.4413	1061.63	1135.71
BP5	12	1000.0 (6.29%)	18.4413	962.959	1037.04
BP50	12	1076.25 (-0.84%)	18.4413	1039.21	1113.29
Diesel	12	1067.17	18.4413	1030.13	1104.21
n [rpm]					
2000	20	1164.25	14.2846	1135.56	1192.94
2250	20	1057.65	14.2846	1028.96	1086.34
2500	20	953.95	14.2846	925.259	982.641
Torque [Nm]					
20	15	537.067	16.4944	503.937	570.197
40	15	841.333	16.4944	808.203	874.463
60	15	1209.8	16.4944	1176.67	1242.93
80	15	1646.27	16.4944	1613.14	1679.4

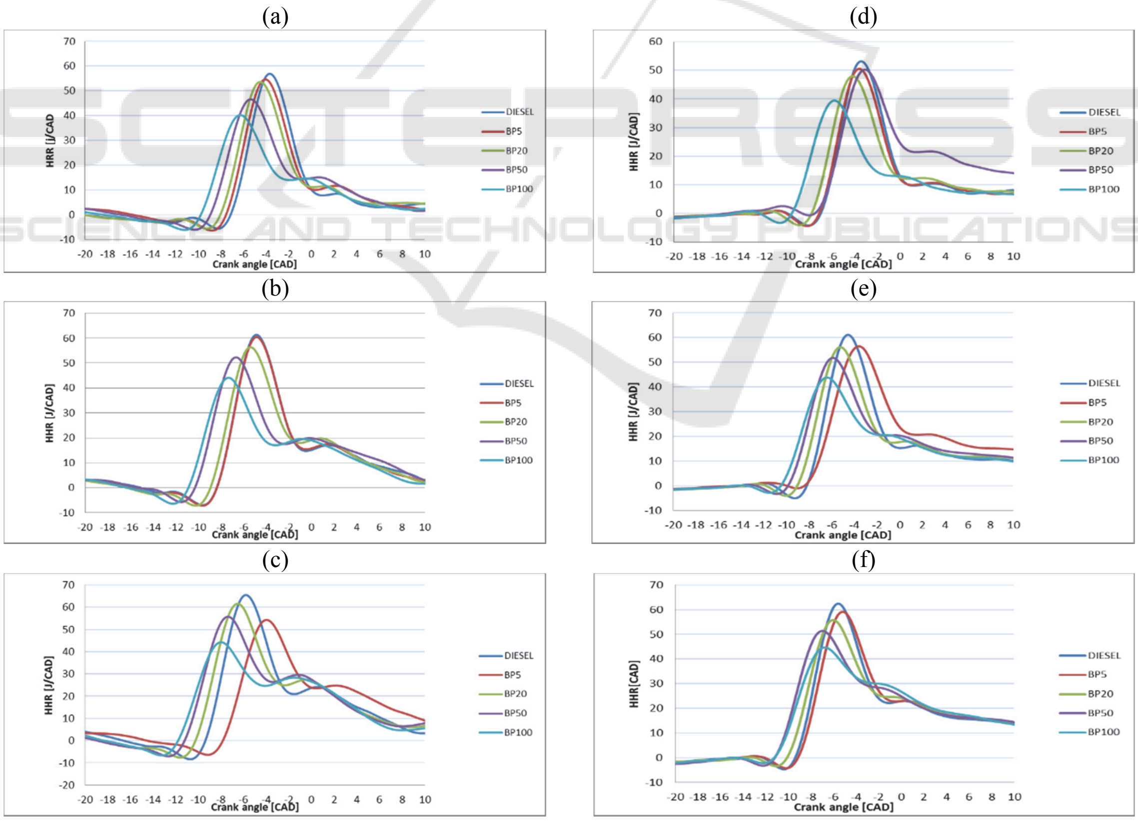

Figure 2: Heat release curves at low loads operating conditions: 20 Nm at (a) 2000 rpm, (b) 2250 rpm, (c) 2500 rpm, and 40 Nm at (d) 2000 rpm, (e) 2250 rpm, (f) 2500 rpm.

Table 6: Maximum mean temperature in the combustion chamber.

		Maximum Mean Temperature [K]				
Torque [Nm]	n [rpm]	Diesel	BP5	BP20	BP50	BP100
20	2000	1277.23	1259.62	1310.14	1339.17	1293.06
	2250	1390.79	1365.97	1419.92	1462.61	1413.00
	2500	1482.81	1420.41	1542.48	1568.07	1513.18
40	2000	1291.93	1254.99	1313.07	1518.04	1300.15
	2250	1423.00	1493.65	1442.08	1494.96	1429.33
	2500	1550.60	1503.25	1562.17	1607.92	1544.56
60	2000	1334.43	1318.25	1339.76	1376.44	1316.89
	2250	1481.05	1450.43	1503.72	1545.67	1487.73
	2500	1659.09	1115.52	1605.96	1608.45	1621.06
80	2000	1531.19	1512.34	1576.29	1407.86	1575.24
	2250	1634.31	1611.54	1607.21	1617.11	1595.88
	2500	1688.41	1611.54	1673.49	1751.85	1681.67

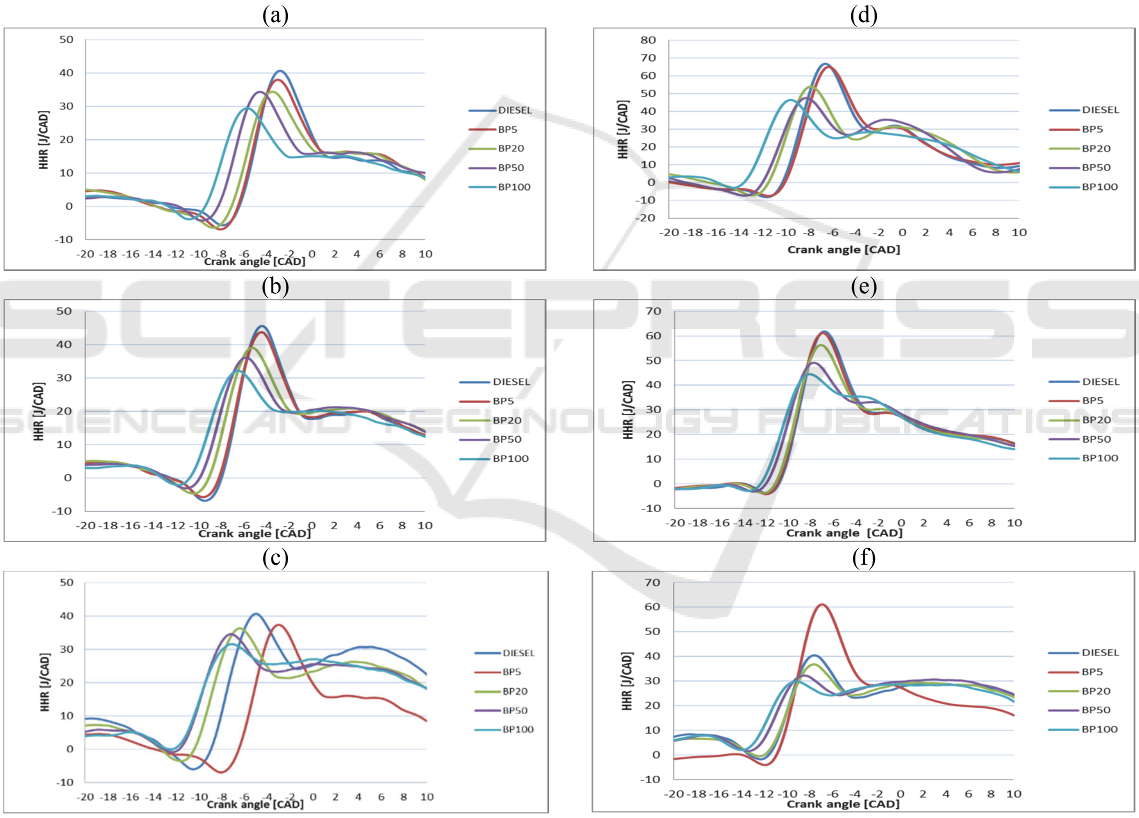

Figure 3: Heat release curves at high loads operating conditions: 60 Nm at (a) 2000 rpm, (b) 2250 rpm, (c) 2500 rpm, and 80 Nm at (d) 2000 rpm, (e) 2250 rpm, (f) 2500 rpm.

behavior is due to the increase of the maximum mean temperature in the combustion chamber as shown in Table 6. The rise of this mean temperature causes the NO_x formation and high loads as presented in the heat release rate curves given in Figures (2) and (3).

Figure 2 presents the heat release rate curves at low engine loads. As observed in this Figure, the combustion premixed phase is predominant for all speeds. As the load increases, the combustion diffusion phase is dominant as presented in Figure 3, in which according to (Dec, 1997) the highest emissions of NO_x are produced.

Finally, the effect of the fuel in NO_x formation did not present a unique trend due to the high sensitivity of the engine to the operating conditions for the blends with palm oil biodiesel. For this reason, it is recommended for future work to determine other physical and chemical properties such as: viscosity, Cetane number and bulk modulus so that the effect of type of fuels blends with palm oil biodiesel can be better understood.

3.2 Semi-empirical Model for NO_x Formation

The equation developed by (Timoney et al., 2005) has been used to establish the theoretical NO_x formation in the combustion diffusion phase.

Table 7: NO_x formation.

Fuel	Experimental NO_x [ppm]	Theoretical NO_x [ppm]	% discrepancy
Diesel	1515	1390	8.25
BP20	1534	1220	20.47
BP50	1461	1420	2.81
BP100	1495	1770	15.54

The operating point at 2500 rpm and 80 Nm was used for calculating the NO_x production thermal mechanism due to its higher combustion diffusion phase. The correlation was not used in the case of fuel BP5 owing to its low combustion diffusion phase. In Table 7 the results are summarized.

4 CONCLUSIONS

Palm oil biodiesel and its blends with diesel produce variations in the NO_x emissions, which increase or decrease according to the engine operation conditions. In general, at high loads the NO_x emissions are increased. This behavior can be explained for the high component of the diffusion combustion phase. At low loads, the premixed combustion phase is predominant, thus resulting in a decrease of NO_x emissions.

The correlations for determining the NO_x formation should include parameters such as: Cetane number, Iodine number in order to get a better estimations taking into account the chemical and physical features of the fuels used.

The combustion processes in diesel engines is highly complex due to the high number of physical and chemical interactions that occur during the operation of the engine. Each phenomenon occurs in tridimensional fluxes, turbulent and non-stationary, interacting with a fuel conformed by complex chains of hydrocarbons. In addition, a detailed chemistry mechanism is unknown for the combustion of palm oil biodiesel.

Lastly, it is necessary to implement optimization techniques for parameter calibration between the experimental and modeled values.

ACKNOWLEDGEMENTS

We would like to thank the GIMEL research group of the Universidad de Antioquia in Medellin for the use of the experimental facilities and advice. Also, we would like to express our acknowledgments to Universidad Cooperativa de Colombia and Istituto Motori of the CNR for their financial support under the project No. 1510 and the Cooperation Agreement No. 0000720. COST (European Cooperation in Science and Technology) Action FP1306 support is also gratefully acknowledged.

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